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- (30) 1997/02/25 (08/806,576) US
- (54) PNEUMATIQUE A FLANC DE CAOUTCHOUC
- (54) TIRE WITH RUBBER SIDEWALL

(57) Pneumatique muni d'un flanc en caoutchouc. Une partie au moins de sa surface extérieure est constituée de caoutchouc blanc dépourvu de renfort de noir de carbone et fait d'un mélange d'élastomère comportant une combinaison de caoutchouc trans -1,4-polybutadiène et de caoutchouc synthétique cis-1,4-polyisoprène sans que ce mélange comporte, sauf en très faible quantité, de caoutchouc naturel cis-1,4-polyisoprène.

(57) A pneumatic rubber tire having a rubber sidewall with at least a portion of its outer surface being composed of white rubber devoid of carbon black reinforcement and composed of an elastomer composition which contains a combination of trans 1,4-polybutadiene and synthetic cis 1,4-polyisoprene rubber and an exclusion of, or substantial exclusion of, natural cis 1,4-polyisoprene rubber.

## Abstract of the Invention

### TIRE WITH RUBBER SIDEWALL

A pneumatic rubber tire having a rubber sidewall with at least a portion of its outer surface being composed of white rubber devoid of carbon black reinforcement and composed of an elastomer composition which contains a combination of trans 1,4
10 polybutadiene and synthetic cis 1,4-polyisoprene rubber and an exclusion of, or substantial exclusion of, natural cis 1,4-polyisoprene rubber.

- 1 -

#### TIRE WITH RUBBER SIDEWALL

#### Field

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This invention relates to a pneumatic rubber tire having a rubber sidewall of which a portion of its outer surface is a white rubber composition.

#### Background

Pneumatic rubber tires conventionally have rubber sidewalls composed of carbon black reinforced rubber compositions which are, therefore, black in color.

Sometimes it is desired to provide a decorative white colored rubber composition on a portion of an outer surface of such tire sidewall. Such rubber composition is conventionally colored white with titanium dioxide pigment and is devoid of, or does not contain, carbon black.

Sidewalls of rubber tires may age somewhat prematurely due to (i) weathering due to atmospheric conditions such as, for example, exposure to ultraviolet light, ozone and high humidity, (ii) fatigue cracking due to continual flexing of the tire sidewall under operating conditions and (iii) abrasion due to scuffing against road curbs or other objects.

White colored tire sidewalls are of special consideration because, (ii) due to the white color of the sidewalls, the weathering, fatigue cracking and abrasion may be more cosmetically observable than for black colored sidewalls and (ii) due to the absence of carbon black reinforcement the white rubber composition (a) before curing has a lower viscosity and, therefore, is a softer composition to process in rubber mixing and extrusion equipment and, also, has a greater tendency to flow which can be a problem for a manufactured article, prior to curing and (b) after curing typically has less abrasion resistance to scuffing.

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In practice, for white sidewalls, weathering is typically retarded by (i) use of antidegradants and, sometimes, the use of low unsaturation rubbers such as, for example, halobutyl rubber - particularly chlorobutyl rubber, and EPDM's, in the rubber composition in the white sidewall rubber composition. EPDM rubbers are well known to those skilled in such art and, generally, mean ethylene/propylene terpolymer elastomers, with a minor amount of non-conjugated diene (e.g. 2 to 15 percent of the terpolymer).

Natural cis 1,4-cis polyisoprene rubber is sometimes used in white sidewall rubber compositions in order to enhance green strength of the uncured rubber composition as well as its building tack and to aid in the processing of the uncured rubber composition during a relatively low shear mixing process typically experienced in mixing the white sidewall rubber composition.

For some white sidewall applications, it is desired to use synthetic cis 1,4-polyisoprene rubber instead of natural cis 1,4-polyisoprene rubber in the white sidewall rubber composition which is, as hereinbefore described, devoid of carbon black reinforcement. While motivation for such substitution may be for a multiple of reasons ranging from (i) concern about visible impurities in natural rubber such as, for example, minor amounts of fiber and dirt impurities from the rubber tree plantation source of the natural rubber to (ii) occasional increased cost considerations for natural rubber as compared to synthetic natural rubber. The fact that the white sidewall rubber is devoid of carbon black reinforcement may also be a motivation because, as hereinbefore discussed, without the carbon black reinforcement, the white sidewall composition is relatively soft and, therefore, processes differently

in mixing and extrusion and typically has less green strength and, therefore, has a greater tendency to flow prior to curing.

However, synthetic natural rubber normally provides less toughness, abrasion resistance and fatigue-to-failure time, than natural rubber for such a white rubber sidewall composition.

Accordingly, it is an aspect of this invention to enable a satisfactory substitution of synthetic cis 1,4-polyisoprene rubber for at least a portion of natural cis 1,4-polyisoprene in a white sidewall rubber composition.

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As will be hereinafter described, such substitution is accomplished by use of a combination of synthetic cis 1,4-polyisoprene rubber and trans 1,4-polybutadiene rubber.

It should be pointed out that it has relatively recently been proposed to use trans 1,4-polybutadiene rubber in tire sidewall compositions, particularly in carbon black reinforced rubber compositions, in order to increase resistance to flex fatigue and tear initiation and/or increase resistance to cut growth.

Considerations of such suggestions of use of trans 1,4-polybutadiene in tire sidewall composition may be found, for example, in U.S. Patent No. 5,386,865.

However, it is not known to the inventor where trans 1,4-polybutadiene rubber is used in a white sidewall rubber composition devoid of carbon black reinforcement where it is desired that the rubber composition contains natural rubber but where a combination of trans 1,4-polybutadiene polymer and synthetic cis 1,4-polyisoprene is used to an exclusion, or substantial exclusion, of natural cis 1,4-polyisoprene rubber.

## Disclosure and Practice of the Invention

In accordance with this invention, a pneumatic rubber tire is provided having a rubber sidewall composed of a carbon black reinforced rubber composition wherein said sidewall also has, as at 5 least a portion of its outer surface, a white rubber composition devoid of carbon black reinforcement, wherein said white sidewall composition is characterized by being comprised of, based on 100 parts by weight rubber (phr), (1) a combination of (A) 10 about 5 to about 30, alternatively about 5 to about 20 phr, of a trans 1,4-polybutadiene polymer, (B) about 10 to about 50, alternatively about 25 to about 45. phr of cis 1,4-polyisoprene rubber(s) composed of 55 to 100, alternatively 70 to 90 weight percent 15 synthetic cis 1,4-polyisoprene rubber and, correspondingly from zero to 45, alternatively from 10 to about 30 weight percent natural cis 1,4polyisoprene rubber, (C) about 40 to about 70, alternatively about 45 to about 65, phr of chlorobutyl 20 rubber and (D) about 2 to about 15, alternatively about 3 to about 10, phr of EPDM as a terpolymer rubber of about 70 to about 25 percent units derived from ethylene, about 28 to about 75 percent units derived from propylene and about 2 to about 15 percent 25 units derived from a non-conjugated diene and (2) about 10 to about 55 phr of titanium dioxide; wherein said trans 1,4-polybutadiene polymer is characterized by having at least a 70 percent trans 1,4-content and at least one melting point within a range of 20°C to 30 60°C.

In one aspect of the invention, said white rubber composition may contain at least one additional rubber in an amount of about 2 to about 15 phr selected from at least one of cis 1,4-polybutadiene rubber, styrene/butadiene copolymer rubber, isoprene/butadiene

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copolymer rubber and styrene/isoprene/butadiene tempolymer rubber.

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In another aspect of the invention, the white sidewall composition may contain about 2.5 to about 15 phr of silica, preferably precipitated silica. If such silica is used, it may also be accompanied by a silica coupler which conventionally has a moiety reactive with silanol groups on the silica surface and another moiety interactive with at least one elastomer in the white sidewall composition.

Significantly, the white sidewall rubber composition is required to be composed of four specified elastomers in specified amounts, namely, the trans 1,4-polybutadiene with its specified Tg and microstructure, the synthetic cis 1,4-polyisoprene rubber, the chlorobutyl rubber and the EPDM rubber. Also significantly, while the rubber composition can optionally contain a fifth elastomer, namely the natural cis 1,4-polyisoprene rubber, so long as it is in the minority insofar as the overall cis 1,4-polyisoprene rubber(s) is(are) concerned.

Thus, in one aspect, the combination of specified, microstructure characterized, trans 1,4-polybutadiene and synthetic cis 1,4-polyisoprene rubber is designed to play a significant role in providing properties similar to or better than the properties typically imparted by natural cis 1,4-polyisoprene rubber and to thereby enable the replacement of, or the substantial replacement of, natural cis 1,4 polyisoprene for a white sidewall composition.

It is important to appreciate that the significance of utilization of the trans 1,4-polybutadiene in the white sidewall rubber composition, where it is desired for the composition to contain natural rubber, is to enable the

replacement of natural cis 1,4-polyisoprene rubber yet provide the toughness, abrasion resistance and fatigue-to-failure properties that natural cis 1,4-polyisoprene rubber, when used, conventionally imparts to a white sidewall rubber composition (devoid of carbon black reinforcement).

Preferably, such trans 1,4-polybutadiene is characterized by having a microstructure of about 75 to about an 85 percent of its butadiene repeat units of a trans 1,4-isomeric structure, about 2 to about 18 percent of its units of a vinyl 1,2-structure and about 2 to about 18 percent of its units of a cis 1,4structure and, in its uncured state, and typically at least one melting point in a range of 20°C to about 60°C. In one aspect, a preferred trans 1,4polybutadiene polymer exhibits two melting points, namely, a first major melting point in a range of about 35°C to about 45°C and a second minor melting point in a range of about 55°C to about 65°C. believed that the said first major melting point is a more significant characterization of the trans 1,4polybutadiene polymer and that the said minor melting point may sometimes be practically non-existent.

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The trans 1,4-polybutadiene utilized by this invention might be prepared, for example, by anionic polymerization by batch or continuous polymerization of 1,3-butadiene in an organic solvent and in the presence of cobalt octoate and triethyl aluminum as a catalyst system with a para alkyl substituted phenol as a catalyst modifier.

For the purposes of this description, the "compounded" rubber compositions refer to the respective rubber compositions which have been compounded with appropriate compounding ingredients such as, for example, carbon black, oil, stearic acid,

zinc oxide, silica, wax, antidegradants, resin(s),
sulfur and accelerator(s).

It is readily understood by those having skill in the art that the rubber compositions of the sidewall would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants, reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

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Typical utilization of titanium dioxide for imparting a significantly white color to a white sidewall rubber composition may comprise about 10 to 55 parts by weight per 100 parts by weight of diene rubber (phr), alternatively about 15 to about 45 phr. It is recognized that typical use of conventional amounts of zinc oxide in the rubber composition also adds a somewhat white color to the rubber composition but not normally the relatively more brilliant white imparted by the titanium dioxide. The titanium dioxide is not considered to be a rubber reinforcing pigment, at least not in the same sense as rubber reinforcing carbon black.

If desired, as hereinbefore discussed, about 2.5 to about 15 phr of silica can be included in the white sidewall rubber composition, optionally together with a silica coupler.

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While commonly employed siliceous pigments used in rubber compounding applications can be used as the silica in this invention, including pyrogenic and precipitated siliceous (silica), precipitated silicas are preferred.

Thus, the siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate.

Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the <u>Journal of The American Chemical Society</u>, Volume 60, page 304 (1930).

The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300.

The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhone-Poulenc with, for example, designations Zeosil 1165MP and silicas designations VN2 and VN3, etc.

While, in the practice of this invention, various silica couplers can be used. Such couplers often

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contain a silane moiety for reaction with silanol groups associated with the silica and another, polysulfide, moiety to interact with at least one of the elastomers in the white sidewall composition. For example, a bis-3-(trialkoxysilylalkyl) polysulfide or bis-3-(trialkoxysilylaryl) polysulfide might be used in which its polysulfide bridge contains about 2 to about 6 sulfur atoms. A preferred coupler is a bis-3-(trialkoxysilylalkyl) polysulfide containing from about 2 to about 8 sulfur atoms in the polysulfide bridge as hereinbefore described. For example, the silica coupler can be bis-3-(triethoxysilylpropyl) tetrasulfide.

Typical amounts of tackifier resins, if used, may 15 comprise about 0.5 to about 10 phr, usually about 1 to about 5 phr. Typical amounts of processing aids may comprise 1 to 20 phr. Such processing aids can include, for example, non staining rubber processing oils. Silica, if used, may be used in an amount of 20 about 5 to about 25 phr, with or without a silica coupling agent. The philosophy of utilization of silica coupling agents to couple precipitated silica to diene-based elastomers for elastomer reinforcing purposes is well known to those having skill in such 25 art. Representative silicas may be, for example, hydrated amorphous silicas, particularly precipitated silicas. Typical amounts of antioxidants comprise about 1 to about 5 phr. Representative antioxidants are, for example, non-staining antioxidants such as phenolic antioxidants as would be well known to those 30 skilled in such art. Various antioxidants for use in rubber compositions are disclosed in the Vanderbilt Rubber Handbook (1978), including pages 344-346. Typical amounts of fatty acids, if used, which can 35 include stearic acid comprise about 0.5 to about 3 Typical amounts of zinc oxide comprise about 2

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to about 6 phr. Typical amounts of waxes comprise about 1 to about 5 phr. Often microcrystalline waxes are used. The presence and relative amounts of the above additives are considered to be not an aspect of the present invention which is more primarily directed to the utilization of the aforesaid specified blends of rubbers, specifically including the combination of the trans 1,4-polybutadiene and synthetic cis 1,4-polyisoprene rubber in white tire sidewall compositions.

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The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from about 0.5 to about 2.0 phr, with a range of from about 0.5 to about 1.5 being preferred.

Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally, a primary accelerator is used in amounts ranging from about 0.5 to about 2.0 In another embodiment, combinations of two or phi: more accelerators which the primary accelerator is generally used in the larger amount (0.5 to 2 phr), and a secondary accelerator which is generally used in smaller amounts (0.05-0.50 phr), in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators have been known to produce a synergistic effect on the final properties and are somewhat better than those produced by use of